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Abiotic Ribose Synthesis Under Aqueous Environments with Various Chemical Conditions

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Abstract

Ribose is the defining sugar in ribonucleic acid (RNA), which is often proposed to have carried the genetic information and catalyzed the biological reactions of the first life on Earth. Thus, abiological processes that yield ribose under prebiotic conditions have been studied for decades. However, aqueous environments required for the formation of ribose from materials available in quantity under geologically reasonable models, where the ribose formed is not immediately destroyed, remain unclear. This is due in large part to the challenge of analysis of carbohydrates formed under a wide range of aqueous conditions. Thus, the formation of ribose on prebiotic Earth has sometimes been questioned. We investigated the quantitative effects of pH, temperature, cation, and the concentrations of formaldehyde and glycolaldehyde on the synthesis of diverse sugars, including ribose. The results suggest a range of conditions that produce ribose and that ribose could have formed in constrained aquifers on prebiotic Earth. Key Words: Ribose—Sugar—Carbohydrate—Formose reaction—Formaldehyde—Pentose. Astrobiology 24, 489–497.

1. Introduction

Carbohydrates are indispensable parts of biomolecules that support bioinformation storage, gene expression, and metabolism on modern Earth. Thus, the origins and availabilities of sugars on prebiotic Earth have been investigated for some time by those interested in the origin of life (Shapiro, 1988; Larralde *et al.,* 1995; Ricardo *et al.,* 2004; Lambert *et al.,* 2010; Kim *et al.,* 2011; Haas *et al.,* 2020). This investigation has extended to the search for carbohydrates in meteorites and extraterrestrial environments (Cooper *et al.,* 2001; Furukawa *et al.,* 2019). These studies continue in various laboratories (Sagi *et al.,* 2012; Roche *et al.,* 2023).

Among different carbohydrate molecules, much research has focused on ribose because this molecule is the sole sugar in RNA, and RNA is seen as a likely primordial informational molecule and biological catalyst (Weiner and Maizels, 1987; Joyce, 1989; Orgel, 2004). Further, quantitative studies in the laboratory have shown that borate offers a mechanism to manage the ''tar paradox'' in allowing controlled maturation of simple carbohydrates (formaldehyde and trace glycolaldehyde) to give pentose carbohydrates (Kim *et al.,* 2011).

This geological model includes the emission SO_2 from a mantle that has a quartz-fayalite-magnetite (QFM) fugacity. This allows these carbohydrates to be delivered as their bisulfite addition products, which are stable against forward reactions. These represent organic mineral feedstocks (Kawai *et al.,* 2019). This model also identifies geological environments where (i) ribose, borate, diamidophosphate, and nucleobase may be converted to nucleoside phosphates; (ii) nucleosides may be converted to nucleoside triphosphates; and (iii) polyribonucleic acid may be formed from triphosphates over basalt, which was also abundant in the Hadean (Kim and Benner, 2017; Benner *et al.,* 2019; Kim and Kim, 2019; Jerome *et al.,* 2022). This laboratory work is complemented by evidence that meteorites contain ribose (Furukawa *et al.,* 2019). This observation suggests that the natural world has a way of making ribose while avoiding the

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''tar paradox,'' the unconstrained devolution of carbohydrates at higher pH values to give complex mixtures.

Missing from this research thread are analyses relevant to the question: How do these carbonyl compounds chemically evolve in the absence of borate and at pH values that are more neutral than the highly alkaline conditions used in many laboratory experiments, largely because higher pH environments allow enolization chemistry to proceed at convenient rates? The second point is important, since any constrained Hadean aquifer in contact with a Hadean atmosphere rich in CO_2 cannot have a very high pH, even if it is eroding alkaline basalt.

This analysis must start with simple chemistry. Processes that ''fix'' formaldehyde (HCHO) molecules by aldol reactions with enolizable carbohydrates in alkaline solution are well known (Breslow, 1959; Shapiro, 1988; Cleaves, 2008). In particular, such aldol reactions are central to the formose processes, where a broad spectrum of sugars are formed from pure HCHO molecules in the presence of calcium hydroxide.

HCHO is, however, not itself enolizable. Thus, conventional chemistry offers no ''polar'' mechanisms that allow the formation of a C-C bond between two HCHO molecules to give an enolizable species, such as glycolaldehyde; there is no way to get the formose process started. This, in turn, makes the initiation of the formose process very, very slow. Thus, when pure HCHO is used on the original formose process (Butlerov obtained it from diiodomethane), single molecule exotic chemistry is required to get the process started (Butlerow, 1861; Ricardo *et al.,* 2006; Eckhardt *et al.,* 2018; Spacek *et al.,* 2023). This may even involve high-energy ionizing radiation.

Once enolizable species are present, subsequent steps that give a rich diversity of carbohydrate products are much faster. This combination of a very slow initiation step followed by very much faster steps that give a more interesting diversity of sugars makes quantitative analyses of the formose process very difficult (Weiss *et al.,* 1970; Tambawala and Weiss, 1972; Weiss and John, 1974; Shigemasa *et al.,* 1977; Shapiro, 1988).

In a prebiotic context, this is not a problem. Formaldehyde was undoubtedly made by photochemical reaction in the atmosphere of Hadean Earth (Pinto *et al.,* 1980). This number may be adjusted based on new ideas of solar energy fluxes and atmospheric chemistry process. However, HCHO formation is indisputable, even with a ''faint early Sun.'' HCHO formation exploits high-energy UV radiation. Thus, the young Sun was perhaps only 70% as bright as it is now, but it was a much larger source of nonthermal radiation, including vacuum UV and X-rays, by factors of 10–100 (Zahnle, 2006).

Various estimates have been made for the amounts of sugars that might have been made from the HCHO, perhaps 10^{-3} M in 10^{7} years in a global ocean (Pinto *et al.,* 1980). Many of these estimates do not consider the discussion above; they are based on an experiment that observed polymerization of pure HCHO in a highly alkaline solution (Ponnamperuma, 1965). Thus, in highly alkaline solutions, neither HCHO nor sugars can accumulate to any significant amounts.

The modern solution to this conundrum takes into consideration that the same photochemistry that produces HCHO also produces its two-carbon isomer, glycolaldehyde ($HOCH_2CHO$). The amounts of glycolaldehyde produced are small, perhaps one part per million (Harman *et al.,* 2013). However, since glycolaldehyde can enolize, it can fix a molecule of HCHO. The resulting product, glyceraldehyde, is *also* enolizable and, thus, can fix *another* molecule of HCHO. Many have now studied the cascade of reactions that follow and form specific sugars in alkaline solutions (Shapiro, 1988; Ricardo *et al.,* 2004; Kim *et al.,* 2011).

In the presence of borate minerals, 5-carbon sugars (ribose isomers) are stopping points. Borate, in turn, was very likely present on the Hadean surface. This was not clear when borate was first introduced into prebiotic chemistry (Scorei, 2012). Indeed, Hazen *et al.* (2011) questioned whether early Earth could have locales with sufficient borate concentrations to be usefully productive (Grew *et al.,* 2011). Because of its high neutron cross section, boron is not produced in stars but rather by spallation. Thus, its abundance is low. While modern Earth has places (*e.g.,* Death Valley) with high borate concentrations, Grew *et al.* (2011) argued that these concentrations could arise only by plate tectonics, which was not sufficiently advanced in the Hadean to provide the fractionation in the crust needed to concentrate borate.

This objection was contradicted by noting that borate is lithophilic and is concentrated in the crust. Further, as a ''bad'' mineral-forming element, it is concentrated in residual igneous melts. From there, it easily erodes, where it fractionates in the hydrosphere. Thus, borate tourmalines are known to have occurred in 3.5 Ga rocks, as established by van Kranendonk, and are much older than the oldest rocks disclosed by Grew *et al.* (2011). Completing the rebuttal, borate was observed on the surface of Mars in prebiotically useful concentrations, even though Mars has never had significant plate tectonics (Gasda *et al.,* 2017). Thus, the issue is largely settled (Furukawa and Kakegawa, 2017; Morrison *et al.,* 2018; Franco *et al.,* 2023).

Recently, a quantitative analysis of sugar molecules in meteorites that might have been formed by formose reaction was reported (Furukawa *et al.,* 2019). In this analysis, each sugar is derivatized into an aldonitrile acetate and thus appears as a peak in gas chromatography–mass spectrometry (GC-MS). These studies detected ribose in those meteorites. This, in turn, suggests that laboratory processes whereby large amounts of HCHO interact with trace amounts of catalytic glycolaldehyde might have a natural correlate. *Ribose and other 5-carbon sugars may have been available on Hadean Earth.*

This inference provides strong motivation to now explore the ''universe'' of products that emerge when HCHO interacts with sub-stoichiometric glycolaldehyde, especially in different geological environments. Very detailed studies have been done on these processes in the presence of borate (Kim *et al.,* 2011). This creates a need for a corresponding exploration in the absence of borate. This exploration is more difficult, as product mixtures are more complex when formose-type reaction processes are not constrained by borate complexation. Here, we report results of such exploration. We again rely on analyzing aldonitrile acetate derivatives with GC-MS to manage the greater complexity.

2. Method

Formose-type reaction experiments in the absence of borate were conducted in a PTFE bottle with HCHO (FA) and glycolaldehyde (GA) using 15 mL of 0.2 mol/L sodium phosphate buffer ($5.7 < \text{pH} < 7.6$) or pure water (pH 4.5). The initial pH values were measured both at an ambient temperature and at the initial reaction temperature, but they were not different. These pH values were only different in experiments without buffers. The experiments were conducted with continuous stirring at fixed temperatures. For comparison, several experiments were conducted with calcium chloride ($CaCl_2$ $2H_2O$) in pure water solvent.

Aliquots (1 mL) of the incubated solution were collected at scheduled incubation times (10, 30, 60, 120, 180, 240, 360 min). Solutions were dried at 25°C under vacuum, dissolved in methanol, and then dried again. This dried sample was derivatized into aldonitrile acetates as described in a previous study (Furukawa *et al.,* 2019).

The derivatized samples were analyzed by Shimadzu GCMS-QP2010 with an Agilent DB-17ms fused silica column (60 m, 0.250 mm, 0.25 μm). The temperature of the injector was 250°C. The column flow, total flow, and split ratio were 0.8 mL/min, 11.8 mL/min, and 10, respectively. The temperature of the column oven was programmed as follows: initial temperature of 50°C for 2 min, then ramp up at 15°C/min to 120°C (hold 5 min), 4°C/min to 160°C, 3°C/min to 195°C (hold 15 min), and 3°C/min to 240°C (hold 10 min).

All chemicals for experiments were used as delivered by suppliers without further purification. Water was prepared by Millipore Milli-Q Integral (<5 ppb TOC and 18.2 MΩ cm^{-1}). Formaldehyde solution (37%; Wako), glycolaldehyde dimer (Sigma-Aldrich), NaH_2PO_4 (Wako), Na_2HPO_4 (Wako), and $CaCl_2$ $2H_2O$ were used as starting materials. For standards of GC-MS analysis, D-ribose, D-arabinose, D-xylose, D-lyxose, and DL-glyceraldehyde were from Wako. Threose, erythrose, L-ribulose, and D-xylulose were from Sigma-Aldrich. D-glucose (Wako), D-mannose (Kanto Chemicals), and D-galactose (Kanto Chemicals) were used as well. (3*S*)-3,4-dihydroxy-2-(hydroxymethyl)butanal (erythro branched pentose), (3*R*)-3,4-dihydroxy-2-(hydroxymethyl)butanal (threo branched pentose), and 1,2,4,5-tetrahydroxy-3-pentanone (pentane-3-one) were prepared as described in a previous study (Kim *et al.,* 2011).

3. Results

Glyceraldehyde, tetroses (threose and erythrose), pentoses (ribose, lyxose, arabinose, xylose), and hexoses (glucose, mannose, and galactose) were formed in mixtures of formaldehyde and glycolaldehyde (Fig. 1). Apiose and pentane-3-one were not detected. Other sugars, deoxy sugars, sugar acids, and sugar alcohols were not investigated. Yields of the investigated sugars differed depending on different mixing ratios of aldehydes, different temperatures, and different pH levels.

The product amounts of these sugars were increased in the following order: glycolaldehyde, tetroses, branched-pentoses (BP) (*i.e.,* threo-BP and erythro-BP), keto-pentoses, aldopentoses, and hexoses, whereas these sugars decreased in the following order: glycolaldehyde, tetroses, and keto-pentoses then other pentoses and hexoses (Fig. 2).

Among pentoses, ketopentoses (*i.e.,* ribulose and xylulose) and branched aldopentoses (*i.e.,* threo-BP and erythro-BP) were formed in higher amounts than linear aldopentoses (Fig. 2). The amounts of ketopentoses were subsequently

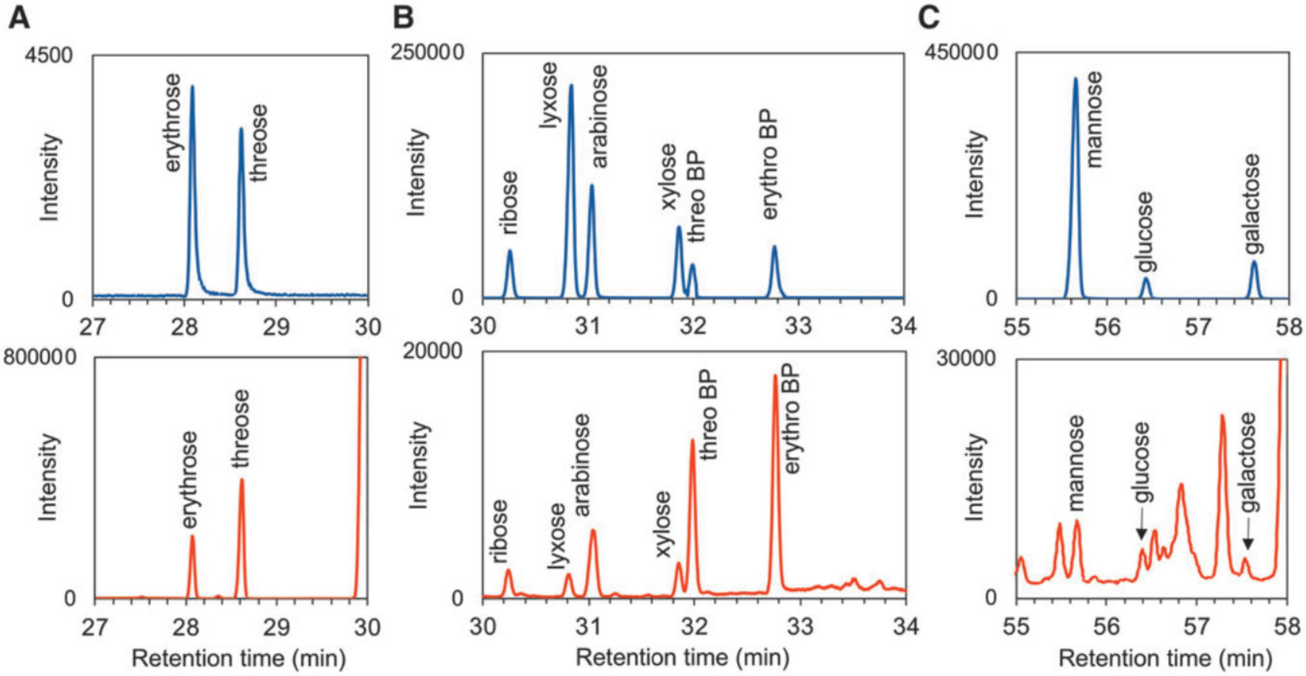

FIG. 1. Gas chromatography–mass spectrometry single ion chromatograms ($m/z = 145$) of product sugars. (**A**) Tetroses. (**B**) Pentoses. (**C**) Hexoses. Upper panels represent commercial standards. These sugars were formed from 100 mM formaldehyde and 10 mM glycolaldehyde incubated at 95°C in a sodium phosphate buffer (pH 7.6). See derivatization methods to explain the $m/z = 145$.

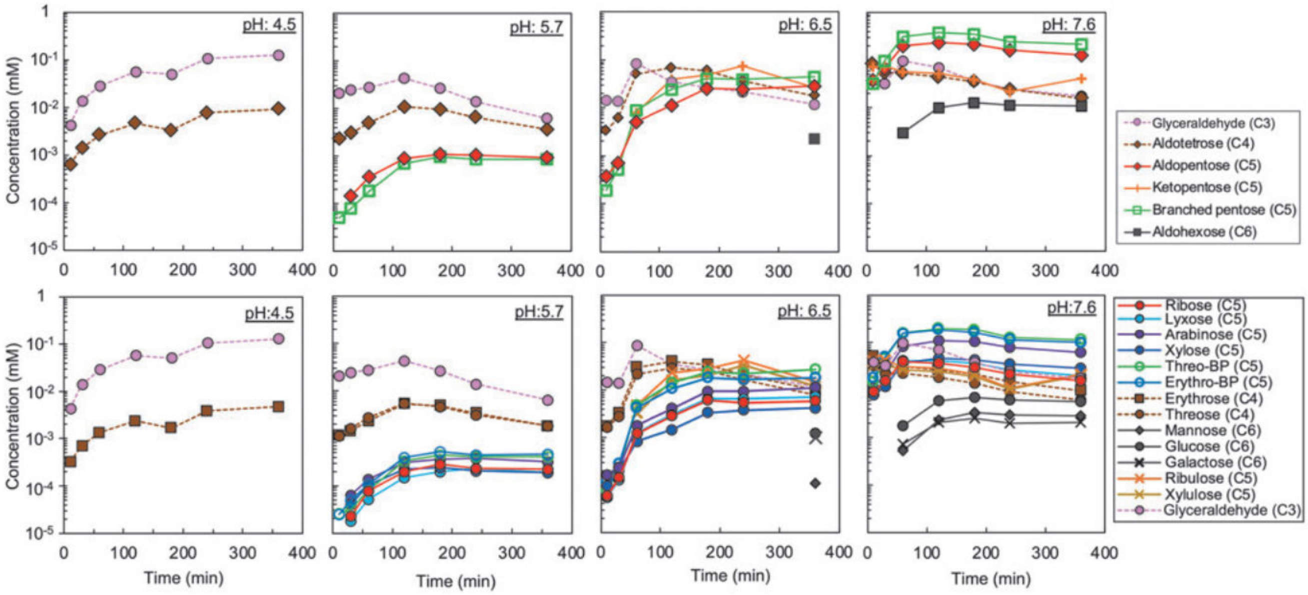

FIG. 2. Effects of pH on the yields of sugars upon reacting 100 mM formaldehyde and 10 mM glycolaldehyde at 95°C. The pH between 5.7 and 7.6 was buffered with sodium phosphate, while the experiment at pH 4.5 (at ∼95°C) was not adjusted with buffer. The pH values dropped by 0.1–0.3 and 1.3–1.5 after the experiments started at 7.6/6.5 and 5.7/4.5, respectively.

decreased while that of branched and linear aldopentoses remained constant for a while.

The maximum yield of ribose increased approximately 10 times with a change of pH from pH 5.7 to 7.6 (Fig. 2 and 3A). This is likely because the enolization of aldehydes increased with the increased pH. Thus, this study shows for the first time (to our knowledge) the formation of ribose from aldehyde solutions at neutral to moderately acidic pH.

The concentrations of glycolaldehyde substantially affected the formation of sugars. Increasing glycolaldehyde tenfold gave 10 times greater maximum concentration of ribose when the amounts of glycolaldehyde in the starting solution were less than that of formaldehyde (Fig. 3C, 3D).

The increase in reaction temperature provided minor effects in the maximum yield of ribose, although the reaction rate was substantially affected (Fig. 4). Lower concentrations of aldehydes provided lower concentrations of

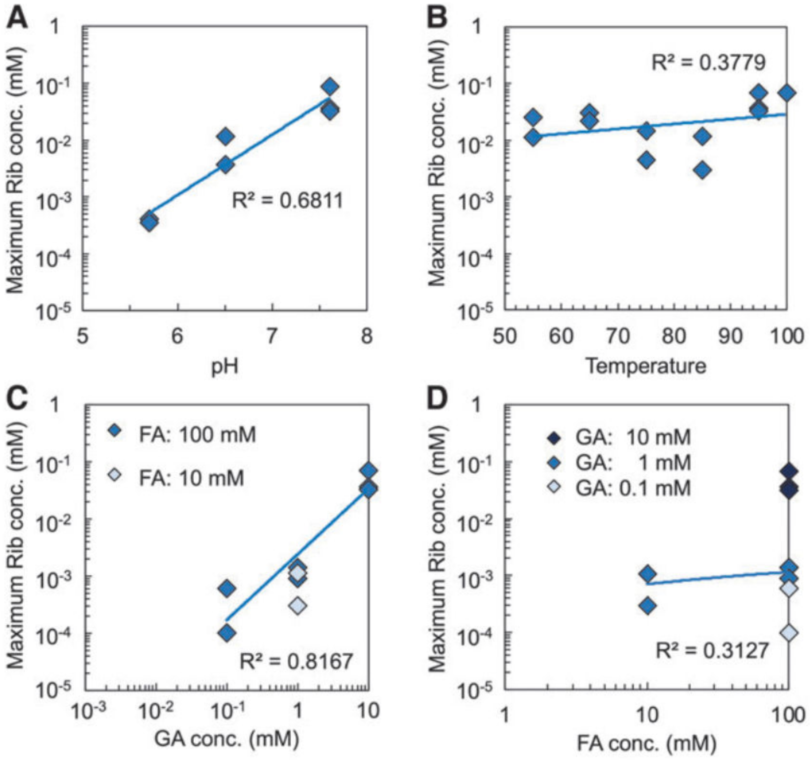

FIG. 3. Maximum yields of ribose in the formose-type reaction. (**A**) Effects of pH. (**B**) Effects of reaction temperature. (**C**) Effects of GA concentrations. (**D**) Effects of FA concentrations.

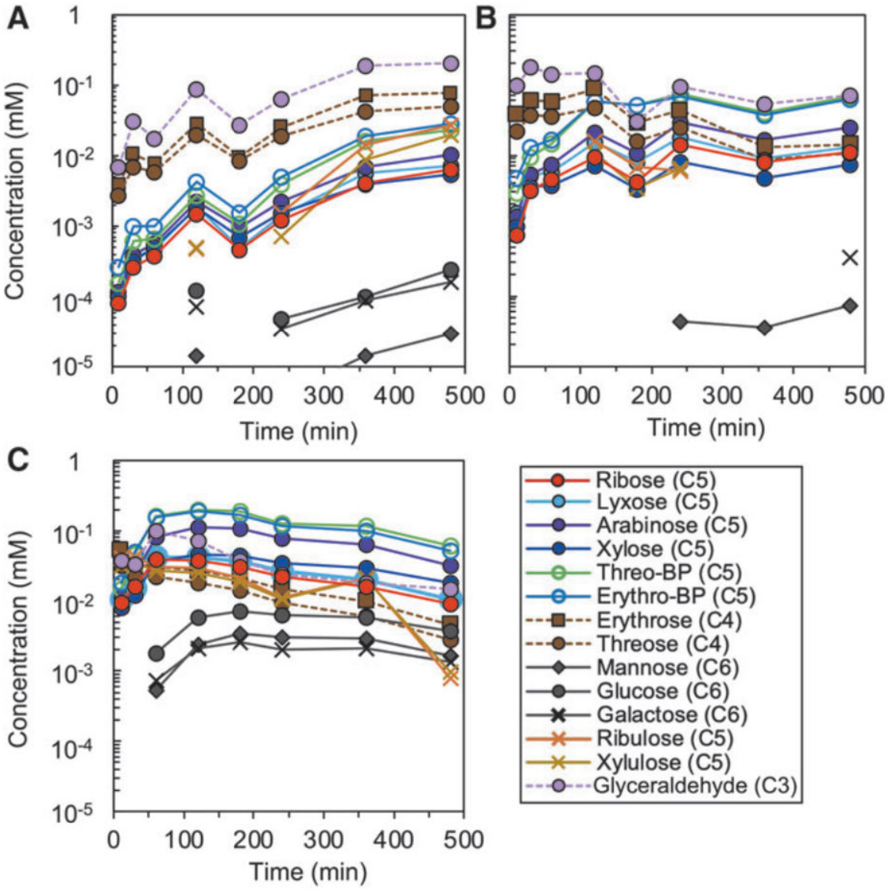

FIG. 4. Effects of temperature on the yields of sugars in the reaction (100 mM formaldehyde and 10 mM glycolaldehyde) at pH 7.5: (**A**) at 55°C, (**B**) at 75°C, (**C**) at 95°C.

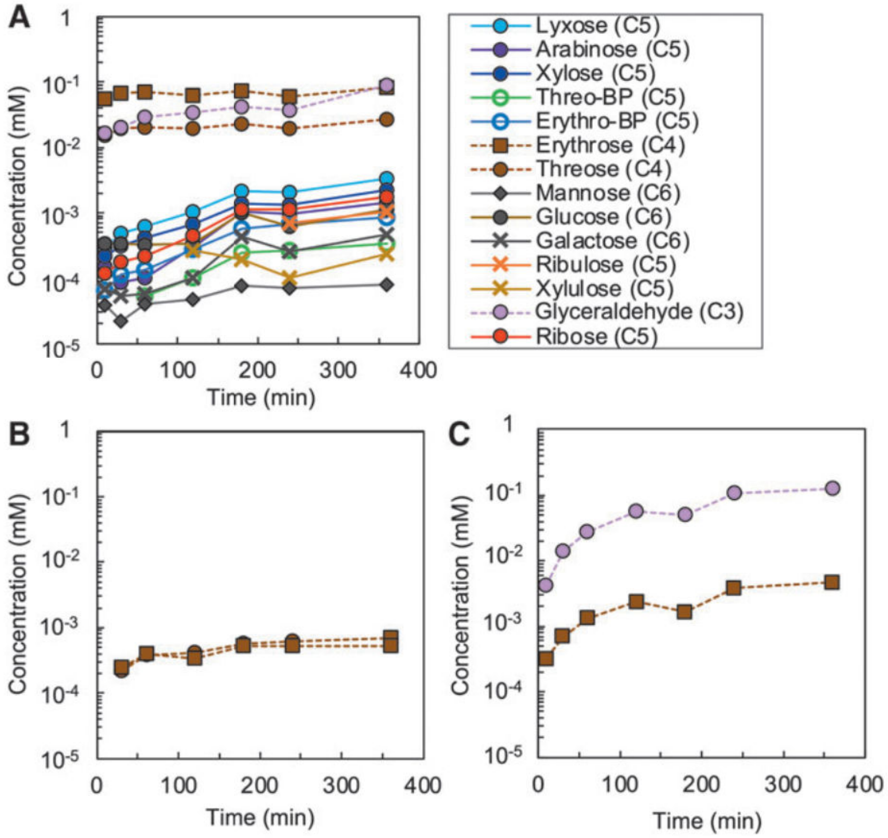

FIG. 5. Effects of calcium and sodium on the yields of sugars in the formose-type reaction (100 mM FA and 10 mM GA) at 95°C: (**A**) in 40 mM $CaCl_2$ solution, (**B**) in 40 mM NaCl solution, (**C**) in pure water. The pH of the sample solution was initially 4.1–4.5 and dropped by ∼0.3 after the experiments.

sugars. However, the concentrations in the starting materials did not provide significant effects on the yield of ribose and other sugars (Fig. 3C, 3D).

The presence of Ca^{2+} significantly increased the yields of sugars in the reaction (Fig. 5). Notably, the yields of branched aldopentoses decreased substantially compared to linear aldopentoses when Ca^{2+} was added to the reaction (Fig. 5).

4. Discussion

The reaction orders from small sugars to larger sugars are reasonable for the synthesis of these sugars by successive aldol addition as described in a previous study (Kim *et al.,* 2011) (Fig. 6). Among pentoses, the amounts of ketopentoses were subsequently decreased while that of branched and linear aldopentoses remained constant for a while. Ketopentoses could be consumed by retroaldol reaction forming smaller aldehydes.

The concentrations of glycolaldehyde substantially affected the formation of sugars. This would be because glycolaldehyde can enolize to react with other aldehydes, while formaldehyde cannot enolize to react with each other to form glycolaldehyde by aldol addition. The presence of Ca^{2+} significantly increased the yields of sugars in the reaction (Fig. 5). Calcium has been investigated as an effective catalyst for sugar synthesis in formose reaction (Shigemasa *et al.,* 1977). The ability of Ca^{2+} to catalyze aldol additions by catalyzing enolization has been discussed (Kim *et al.,* 2011). Another study pointed out the effect of calcium to convert ketopentoses into aldopentoses by hydride shift (Appayee and Breslow, 2014). The results of the present study, that is, preferential catalyzation of linear aldopentose formation, are consistent with both of these previous studies.

The pH of early Archean open oceans has been estimated at near neutral to slightly acidic (*i.e.,* pH 6.5–7). These studies have shown that in this pH range ribose would have been formed, although the rate of its formation should be lower than that in higher pH ranges. Thus, this work fills in a gap in this literature. To obtain reactions at rates that are conveniently studied, most work in these areas has been done at higher pH values.

Depending on the overall redox potential of the atmosphere, the ratio of glycolaldehyde to formaldehyde formed

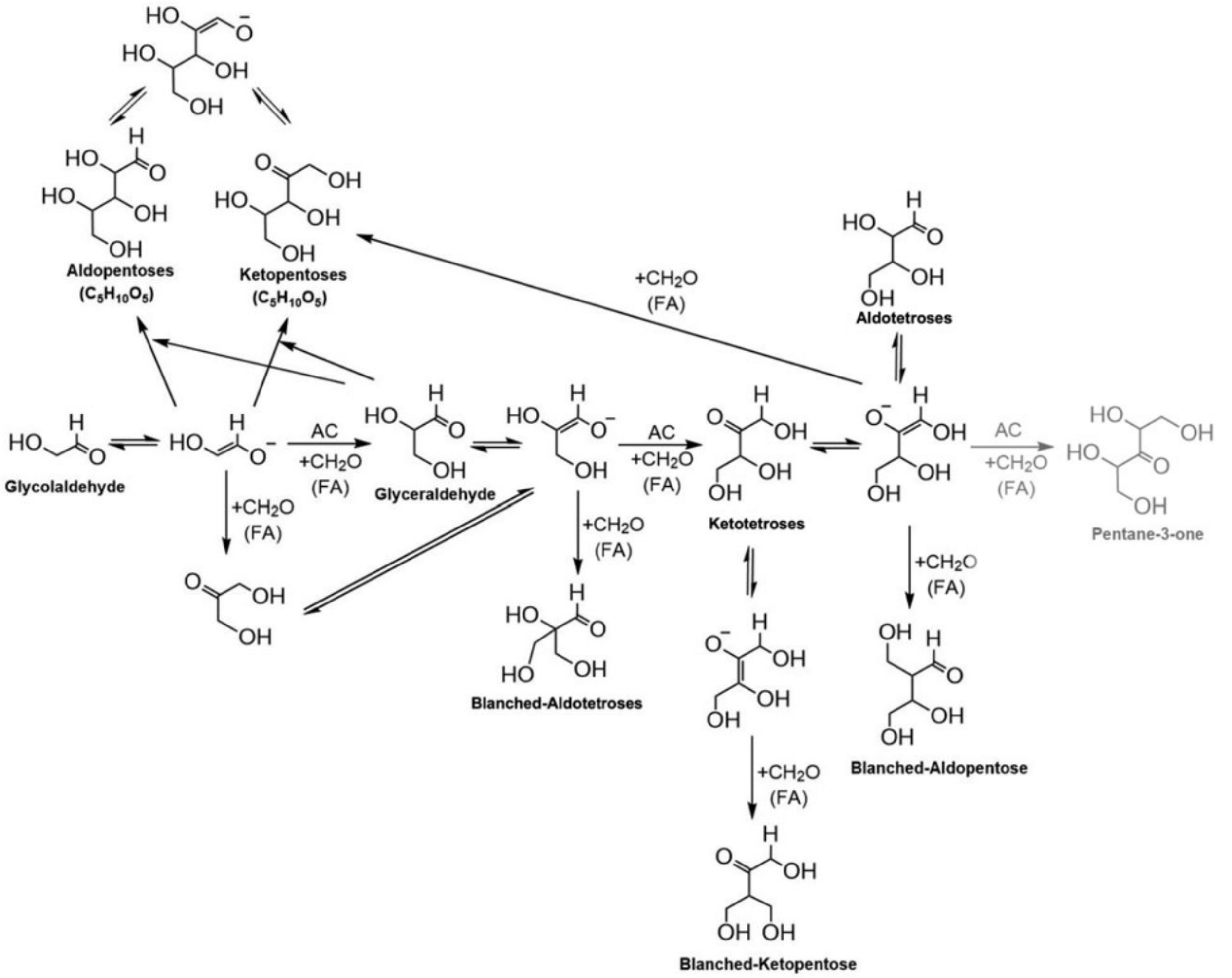

FIG. 6. A selection of possible reactions between enolizable glycolaldehyde, formaldehyde, and subsequent products. Note the possibility of the formation of ketones from aldehydes via an enediolate, called the *Lobry de Bruyn/van Ekenstein* transformation. In detailed studies (Ricardo *et al.* 2006; Kim *et al.* 2011), these are not seen at higher pH values if HCHO is present.

in the Hadean atmosphere is $\sim 10^{-5}$, here for an atmosphere of 0.02 CH_4/CO_2 (Harman *et al.,* 2013); Harman *et al.* used a one-dimensional model for these calculations, as detailed in their paper. For convenience, we explored ∼100 fold higher ratios. This gave an experimental formation of ribose in yields of $\sim 3.5 \times 10^{-4}$ $\mathrm{mol_{Rib}/mol_{FA}}$ from the neutral glycolaldehyde-formaldehyde solution (*i.e.,* 100 mM formaldehyde and 0.1 mM glycolaldehyde). This allowed us to measure the yields of ribose as a function of glycolaldehyde/formaldehyde.

These results suggest that ribose forms $\sim 3.5 \times 10^{-6}$ $\mathrm{mol_{Rib}/mol_{FA}}$ in neutral solutions with the 10^{-5} of glycolaldehyde/formaldehyde in the absence of calcium. Assuming a rainout rate of formaldehyde from the Hadean atmosphere to the surface at 2.8×10^{8} molecules $\mathrm{cm^{-2}\ s^{-1}}$ (Pinto *et al.,* 1980), the yield of ribose would have been 3.5×10^{-6} $\mathrm{mol_{Rib}/mol_{FA}}$, corresponding to the formation 4×10^{26} mol/day of ribose in the neutral ocean. Of course, this material would be more likely useful in constrained aquifers in direct or indirect contact with the atmosphere.

The concentration of calcium in the Hadean ocean is not clear. However, it is reasonable to assume that seafloor weathering or submarine hydrothermal processes may have supplied Ca^{2+} into Hadean oceans through the alteration of Ca-bearing silicates (*i.e.,* plagioclase) into clays. The dissolved Ca^{2+} in the Hadean ocean would have further promoted ribose synthesis, enhancing recycling of ketopentoses and branched aldopentoses to form smaller aldehydes that have potential to rearrange to form linear aldopentoses, including ribose (Fig. 5).

Other sources of glycolaldehyde and formaldehyde are extraterrestrial delivery by carbonaceous chondrites and synthesis by bolide impacts of iron-rich asteroids/meteorites (Aponte *et al.,* 2019; Masuda *et al.,* 2021). Aldehydes provided by these processes may have formed large amounts of additional sugars in local areas where the impact happened.

These sugars formed globally and locally would be consumed by further reactions in the timescale of several days (∼90°C) to several weeks (∼50°C); they are unlikely to have accumulated for 10^7 years, as a previous study estimated (Fig. 4). Environments rich in borate and boric acid would contribute to the accumulation substantially because borate increases the stability of ribose, binding to its diols and preventing further reactions related to aldehyde (Prieur, 2001; Ricardo *et al.,* 2004; Scorei and Cimpoiasu, 2006; Furukawa *et al.,* 2013).

Ribose formed by the reactions could be used for further chemical evolution to form nucleotides. Borate is also known to contribute to many steps in forming ribonucleotides abiotically (Furukawa *et al.,* 2015a; Kim *et al.,* 2016; Becker *et al.,* 2019; Hirakawa *et al.,* 2022; Takabayashi *et al.,* 2023). However, formation of nucleobases and their precursors that are needed to form ribonucleotides on Hadean Earth would need other reduction mechanisms for nitrogen, such as impacts of iron-rich asteroid/meteorites (Furukawa *et al.,* 2014, 2015b; Benner *et al.,* 2020; Peters *et al.,* 2023) and deep-sea hydrothermal systems (Summers and Chang, 1993).

Needless to say, this work focuses on RNA (not DNA) as the first genetic molecule. DNA is also a topic of discussion (Teichert *et al.,* 2019). Likewise, we focus on HCHO and glycolaldehyde as the feedstocks, since these could not *not* have been formed in the Hadean atmosphere, and stabilized as bisulfite addition products, which form organic minerals. However, the literature contains an explosion of interesting alternative ideas for prebiotic ribose and nucleoside formation that rely on carbohydrate feedstocks with higher molecular weights and formed off-planet (Eckhardt *et al.,* 2018; Kruse *et al.,* 2020).

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Abbreviations Used

BP = branched-pentoses
FA = formaldehyde (HCHO)
GA = glycolaldehyde
GC-MS = gas chromatography–mass spectrometry